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(54) **Method of synthesis of polyaminofunctional hydroxyurethane oligomers and hybride polymers formed therefrom**

(57) Chemically resistant materials with high mechanical properties are provided by using adducts of primary diamines (with oligocyclocarbonate and epoxy

compounds) and epoxy oligomers with ended epoxy groups (or mixture of epoxy oligomers and oligomercaptanes).

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Description

Technical Field

[0001] The present invention is related to epoxyurethane oligomers without isocyanates and polymer compounds based on them and, more specifically, to coatings, adhesives, composite materials, sealants, synthetic leather and to methods of producing such materials.

Background of the Invention

[0002] It is known method of preparing polymers by using aminourethane oligomers (without requiring the use of isocyanates) and an epoxide resin to form hardener crosslinked polymer (USA patent 5175231, published Dec 29, 1992).

But it is impossible to prepare nonisocyanate polyurethane-epoxyde materials using mixture containing both epoxy and cyclocarbonate groups because of simultaneously reactions of epoxy and cyclocarbonate groups with the primary amino groups. So far as cyclocarbonate groups react only with primary aminogroups many cyclocarbonate groups do not react. So in such mixture after hardening cyclocarbonate compounds only plasticize the epoxy polymer and it is impossible to prepare epoxy-polyurethane materials with high properties.

Summary of the Invention

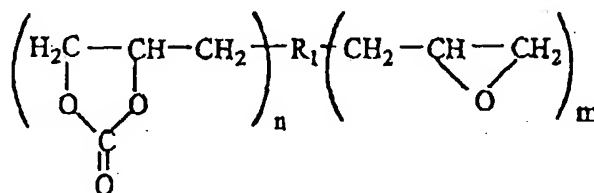
[0003] One embodiment of the present invention relates to oligomers containing epoxy and cyclocarbonate groups, adduct of aliphatic or cycloaliphatic diamines with these oligomers. Such oligomers may be used for curing epoxy resins, for preparing constructive glues, sealants, coatings, construction, etc.

Detailed Description of the Invention

[0004] Polyfunctional oligomers of the present invention are based upon oligomers with epoxy and cyclocarbonate groups, which was prepared by the reaction of carbon dioxide and an epoxy oligomer with catalizer according our pat. (Patent Israel 122763).

[0005] Such oligomers containing epoxy and cyclocarbonate groups react with aliphatic or cycloaliphatic amines by epoxy and cyclocarbonate groups. These adducts are used as hardeners for epoxy oligomers or mixture of epoxy oligomers and oligomercaptanes.

[0006] For preparing epoxy-polycyclocarbonate adduct are used epoxy-cyclocarbonate oligomers preferably of such formula:



[0007] Suitable commercially available epoxy resins

DER-324, DER-332, DEN-431 EPON 813, EPON 8021, EPON 8091, EPON 825, EPON 828 NPEF-165 PEP 6180, PEP 6769, PEP 6760 Araldite 0510, MY-0501, MY-720 Laprolat 803, 703 Ricotuff 1000-A, Ricotuff 1100-A,	Dow Chemical Co (USA), Shell Chemical Co (USA), Nan Ya Plastic Corporation (R. China), Pacific Epoxy Polymers, Inc(USA), Ciba-Geigy A.G. (USA), "Macromer" Ltd. (Russia),
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(continued)

Ricotuff 1110-A, Ricopoxy 30
Setalux AA-8502, 8503
Eponex 1510, 1511

Ricon Resins, Inc. (USA),
AKZO NOBEL (Netherland),
Shell Chemical Co. (USA).

[0008] Preferably commercially available primary amines: N,N-bis(3-aminopropyl) methylamine (BASF, Germany), m-xylylenediamine (Mitsubishi, Japan), triethyleneglycoldiamine (Jeffamine), EDR-148 (Huntsman Corporation, USA), 1,3-diaminopentane (Du Pont, USA), Isoforodiamine (BASF, Germany), Jeffamine T-403 (Huntsman Corporation, USA), etc.

Examples

[0009] The following examples of polyaminofunctional urethane oligomers and hybride polymers formed therefrom. However, it is to be understood that the examples are for illustrative purposes only and in no manner is the present invention limited to the specific disclosure therein.

Example 1: Preparing Polyaminofunctional urethane Oligomers

[0010] Ten sample compositions of the invention were prepared by the following method. The components formulated into each sample and the amounts used are shown in Table 1.

[0011] Synthesis is a reaction between epoxy and cyclocarbonate groups with polyamines. Such process is working out in special glass reactor under N_2 . Contents are mixed during 10 min at the 20°C, after that the reaction continues during 0,5-1 hr by 80-120°C (or 24 hrs by 20-25°C). After this operation according with Table 1 oligomers are mixed with epoxy resins for curing (according Table 1) with adding fillers and pigments or without.

[0012] After that the reaction of curing continues during 2 hrs by the 110-120°C or 7 days at 20°C.

[0013] For preparing coatings were used 80% solutions in butylglycol or dimethylformamide.

[0014] Additionally, certain control samples were also prepared by the above method.

[0015] **Composition 1c** is identical to Composition 1 except that epoxy-cyclocarbonate oligomer with EEW = 331; CC EW = 615.4 was used in the reaction of oligomerisation.

[0016] **Composition 2c** is identical to Composition 1 except that epoxy-cyclocarbonate oligomer with EEW = 653; CC EW = 352 was used in the reaction of oligomerisation.

[0017] **Composition 3c** is identical to Composition 3 except that epoxy-cyclocarbonate oligomer with EEW = 248; CC EW = 744 was used in the reaction of oligomerisation.

[0018] **Composition 4c** is identical to Composition 4 except that epoxy-cyclocarbonate oligomer with EEW = 2000; CC EW = 240 was used in the reaction of oligomerisation.

[0019] **Composition 5c** is identical to Composition 5 except that epoxy-cyclocarbonate oligomer with EEW = 921; CC EW = 196 was used in the reaction of oligomerisation.

[0020] **Composition 6c** is identical to Composition 6 except that epoxy-cyclocarbonate oligomer with EEW = 161; CC EW = 758 was used in the reaction of oligomerisation.

[0021] **Composition 7c** is identical to Composite 7 except that epoxy-cyclocarbonate oligomer with EEW = 193 ; CC EW = 358 was used in the reaction of oligomerisation.

[0022] **Composition 8c** is identical to Composite 8 except that epoxy-cyclocarbonate oligomer with EEW = 396; CC EW = 213 was used in the reaction of oligomerisation.

[0023] **Composition 9c** is identical to Composite 9 except that epoxy-cyclocarbonate oligomer with EEW = 426; CC EW = 1401 was used in the reaction of oligomerisation.

[0024] **Composition 10c** is identical to Composite 10 except that epoxy-cyclocarbonate oligomer with EEW = 1502; CC EW = 457 was used in the reaction of oligomerisation.

Table 1. Compositions (in parts by weight based on 100 parts cyclocarbonate oligomer)

Composition	1	2	3	4	5	6	7	8	9	10
Epoxy-Cyclocarbonate oligomer based on BPA epoxy resin D.E.R.-324 BEW=444 CC EW=444	100	100	-	-	-	-	-	-	-	-
Epoxy-Cyclocarbonate oligomer based on Novolac Resin DEN 431 BEW=569 CC EW=316	-	-	100	100	-	-	-	-	-	-
Epoxy-Cyclocarbonate oligomer based on Methylen-bis(o-ethylaniline) XUMY-722 BEW=632 CC EW=211	-	-	-	-	100	100	-	-	-	-
Epoxy-Cyclocarbonate oligomer based on aniline PBP 6760 BEW=264 CC EW=264	-	-	-	-	-	-	100	100	-	-
Epoxy-Cyclocarbonate oligomer based on trimethylol propane, oxide propylene, epichlorhydrine BEW=1038 CC EW=519	-	-	-	-	-	-	-	-	100	100
N,N-bis(3-aminopropyl)methylamine Mw 146	65.8		71.7		92			211		

Methylpentamethylenediamine		52.3					73.4					
Mw 116												
Isophorondiamine										46.9		
Mw 170												
Methoxylylenediamine												
Mw 136											37.5	
Jeffamine T-403												
HEW 81					239				362.8			
HEW	184	169	204	158.2	135	122	154.5	139	228.3	213.7		
Epoxy oligomer DER-324												
BEW 200	180.2				284.4		469.6					
Epoxy novolac oligomer DEN 431												
BEW 175		157.7	147.3				248.7	391.5				
Epoxy oligomer Eponox-1510 (Hydried BPA)					450							
BEW 200									135.1	135.1		

Examples 2: Preparing NIPU hybrid coatings

[0025] Cyclocarbonate oligomers (1-10) prepared according the method described in Example 1 were used to coat a cleaned steel plate. Each composition formed a coating layer with a thickness of 1-2 mm. Then the coating was hardened at a temperature 110°C for 2 hours. These coated steel samples were used to determine the adhesion of each coating to the steel substrate according to the method prescribed by ASTM D3359-93. Compositions were used as 80% solution in butylglycol. For the purposes of tensile testing, the above procedure was modified by using a polytetrafluoroethylene (PTFE) sheet instead of steel plate, so a free film of each of the 10 cyclocarbonate-oligomers could be obtained by peeling the PTFE from the cured film. The tensile properties, i.e. tensile strength and elongation at break, of each free cured film were determined according to the method prescribed by ASTM D638-84. Such samples were also used to determine the coefficient of chemical resistance of each coating by the procedure discussed above in which the tensile strength was used to determine K_{CR} .

[0026] The properties of ten coatings of the invention, samples 11-20, are shown in Table 2.

[0027] The properties of ten coatings, samples 21-30, are also formed by the above described method are shown in Table 3.

Table 3: Properties of Cured Control Coatings

[illegible]

[0028] The proposed oligomers may be used for preparing adhesives, sealants, synthetic foams, synthetic leathers, hardeners for epoxy resins, casting elastomers, structure plastics, etc.

[0029] The possible areas of applications are illustrated by following examples. Adhesives based on the compositions 1-10 (table 1) can be used as structure adhesives with high service properties. The adhesives compositions have been received by adding to adducts (1-10) epoxy resins, which are using here as a hardener. Such method of Adhesives preparing gives adhesives joints with more shock and vibration resistance properties. The mechanical properties of adhesives joints were described in the table 2.

[0030] By preparing of adhesives compositions pigments and fillers can be also added. Preferable ones are barium sulfate, titanium dioxide, silica and ferrous oxides pigments and aluminate cement. By adding as a filler glass microspheres can be received synthetic foams.

[0031] Sealants can be received on the base of adducts by example 1, 3, 7. In this case are needed using another hardeners (see table 4). The properties of such sealants are given in the table 5.

[0032] On the base of oligomers according to example 1-10 can be also prepared reinforced plastics with glass, carbon or kevlar fibers and polymerconcretes with high impact, shock and abrasive resistance, with 2-3 times higher mechanical properties than those of well known unsaturated polyester reinforced plastics and concretes.

[0033] For the purposes of fast curing it is possible to use usual accelerators. The above procedure was modified by using an oligomeric mercaptane (polysulfides).

[0034] Four compositions of the invention were prepared by adding oligomercaptane (Capcure 3-800) and epoxy oligomer to the compositions 1.3.5.8 (according table 1) with adding additional amounts of epoxy oligomers.

[0035] Reference is made to table 6 and samples 31-34.

[0036] The curing time of four coatings (samples 31-34) in comparison with analogous samples without accelerator is shown in table 7.

Table 4:

Compositions for Sealants (parts by weight).						
Sample No	21	22	23	24	25	26
Composition	11	12	13	14	15	16
Epoxy Cyclocarbonate oligomer based on BPA epoxy resin DER-324 EEW=444 CCEW=444	100	-	-	100	-	-
Epoxy Cyclocarbonate oligomer based on Novolac Resin DEN 431 EEW=569 CCEW=316	-	100	-	-	100	-
Epoxy Cyclocarbonate oligomer based on aniline PER 6760 EEW=264 CCEW=264	-	-	100	-	-	100
N,N bis(3 aminopropyl) methylamine Mw 146	65.8	71.9	-	65.8	71.9	-
m-Xylenediamine Mw 136	-	-	103	-	-	103
Molecular weight of adduct	736	978	539	736	978	536
HEW	147.2	148	107	-	-	-
Epoxy oligomer D.E.R-732 EEW=320	361 (78%)	372 (79%)	607 (86%)	-	-	-
Epoxy oligomer Ricopoxy 30 EEW=717	-	-	-	809 89%	833 89%	1360 93%

Table 5:

Sealants properties.						
Sample No	21	22	23	24	25	26
Composition	11	12	13	14	15	16
Tensile strength, MPa	60	58	56	46	42	42
Elongation at Break, %	100	110	115	360	400	500

Table 6.

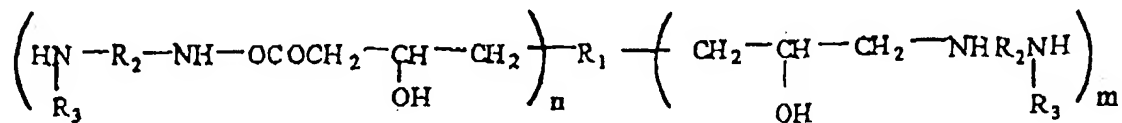
Composition	31	32	33	34
Epoxy-Cyclocarbonate oligomer on BPA epoxy resins DER-324 EEW-444, CCEW-444	100	-	-	-
Epoxy-Cyclocarbonate oligomer based on Novolac resin DEN-431 EEW-569, CCEW-316	-	100	-	-
Epoxy-Cyclocarbonate oligomer based on Methylen-bis(o-eyhtlamine)	-	-	100	-
Epoxy-Cyclocarbonate oligomer based on aniline PEP 6760 EEW-264, CCEW-264	-	-	-	100
N,N-bis(3-aminopropyl)methyl amine	65.8	71.7	92	211
HEW	184	204	135	139
Olygomercaptane Capcure 3-800 EW-270	135	135	135	135
Epoxy oligomer DER-324, EEW-200	280	247	384	491

Table 7.

Curing time of coatings.								
Sample No								
	1	31	3	32	5	33	8	34
Curing time, h	18	2	18	3	18	4	18	4

Claims

1. Polyaminofunctional oligomers



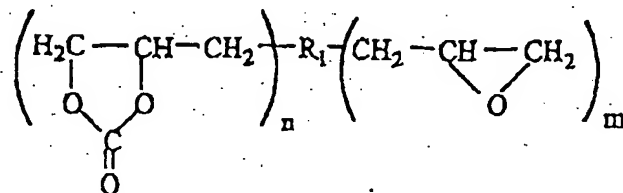
where:

R₁ — aliphatic, cycloaliphatic, oligoester or oligoether radicals

R₂, R₃ — H, alkyl, aryl alkylaryl;

m = 0.1-2; n = 1-5

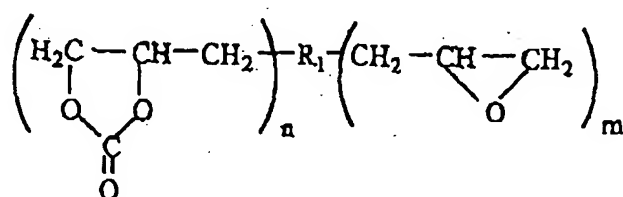
2. The method of preparing of polyaminofunctional oligomers by reaction of compounds



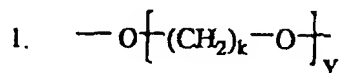
with primary diamines by stoichiometric ratio to epoxy and cyclocarbonate groups.

3. The method according p.2, includes reaction carried out by temperature from 80°C to 120°C both in "situ" and in organic solvents.

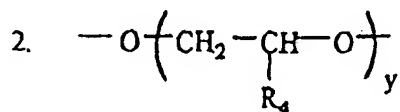
4. The method according claim 2 or 3 includes using oligomers, chosen from the group which includes oligomers having the following structures:



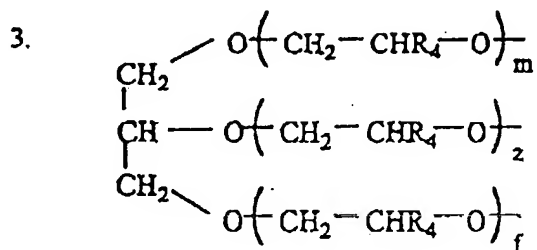
where $\text{R}_1 =$



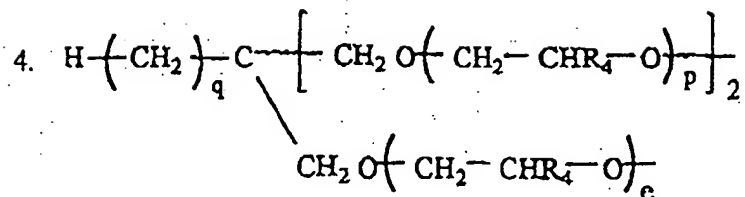
$k = 2 - 6, y = 1 - 20, n = 1$



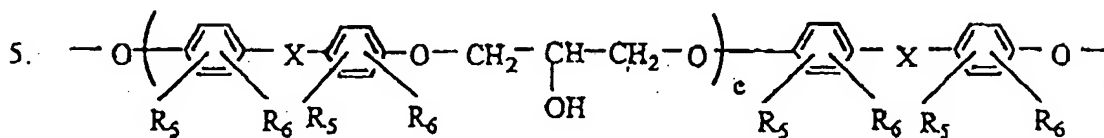
where: $\text{R}_4 = \text{CH}_3, \text{C}_2\text{H}_5$ $y = 1 - 20, n = 1$



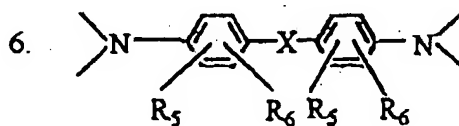
where: $\text{R}_4 = \text{H}, \text{CH}_3$ $m + z + f = 0 - 50$ $n = 2$



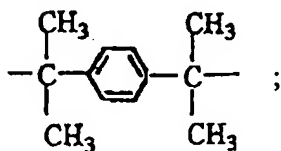
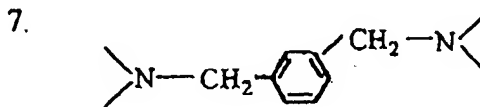
where: $R_4 = H, CH_3$ $p + e = 0 - 50$ $q = 1 - 2$ $n = 2$



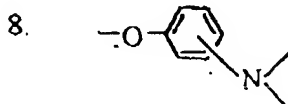
where: $X = -CH_2-$, $(CH_3)_2C<$, $-SO_2-$, $(CF_3)_2C<$; $R_5, R_6 = -H, -CH_3, -Cl, -Br$; $e = 0-5$, $n = 1$

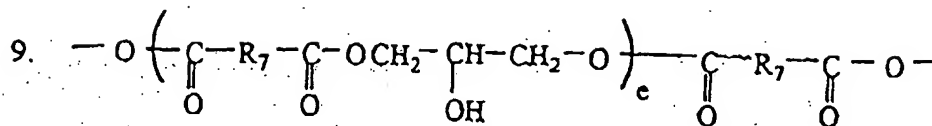


where: $X = -CH_2-$, $(CH_3)_2C<$, $-SO_2-$,

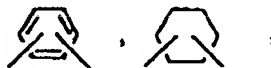

$$R_5, R_6 = -H, -CH_3, -Cl; n = 3$$


n=3

 $n=2$

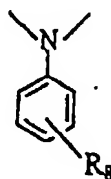


where: $\text{R}_7 =$



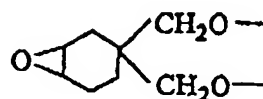
$-(\text{CH}_2)_m-$; $e = 0-2$, $n = 1$

10.

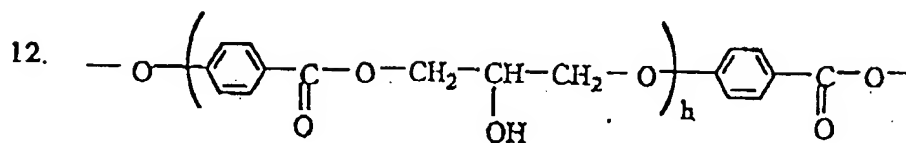


where: $\text{R}_8 = -\text{H}$, $-\text{CH}_3$, $-\text{Br}$, $-\text{Cl}$; $n = 1$

11.

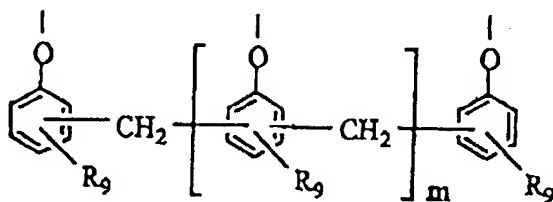


$n = 1$



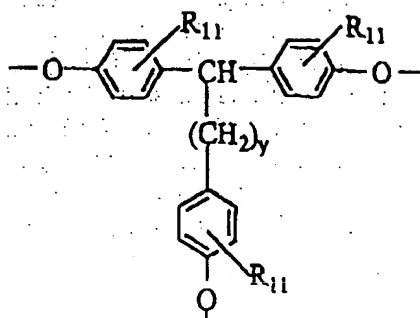
$h = 0-2$ $n = 1$

13.



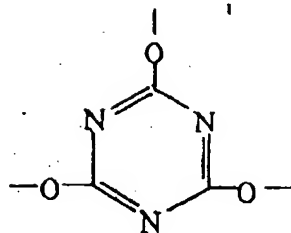
where: $\text{R}_9 = -\text{H}$, $-\text{CH}_3$; $m = 1-5$, $n = 2-6$

14.



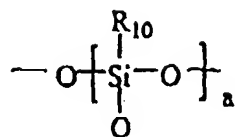
where: $R_{11} = \text{---H, ---CH}_3$; $y = 1 - 2$, $n = 2$


15.



$n = 1$

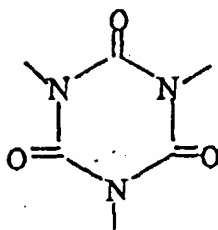
16.



where: $R_{10} = \text{---CH}_3$,  ;

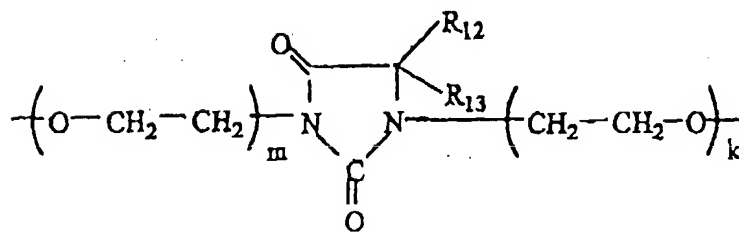
$a = 1 - 4$, $n = 2 - 5$

17.



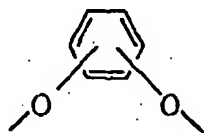
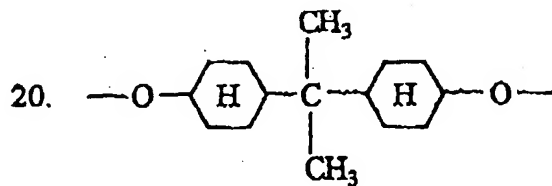
$n = 2$

18.

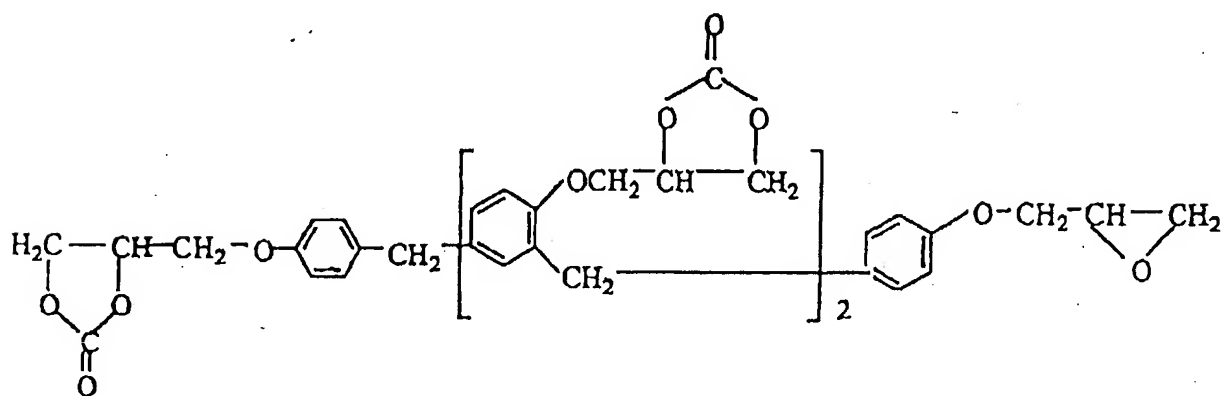
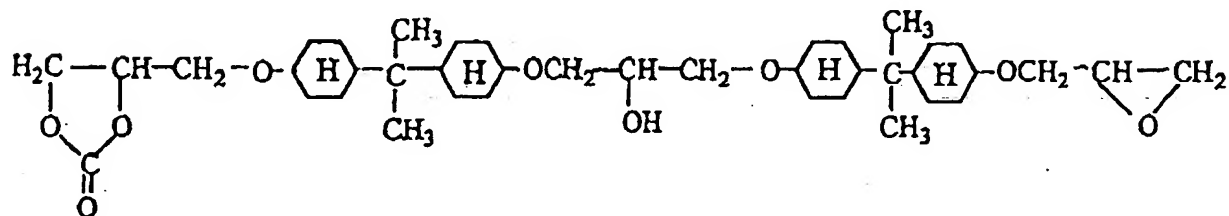
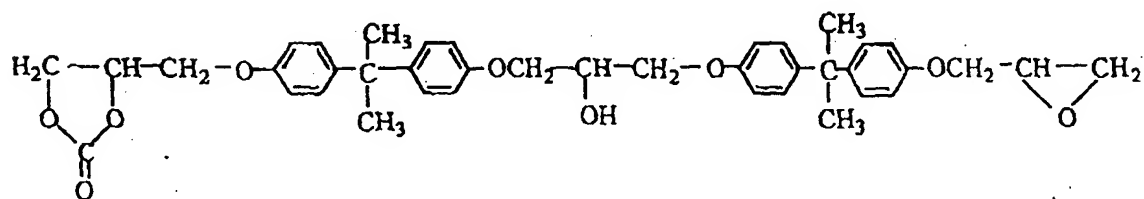


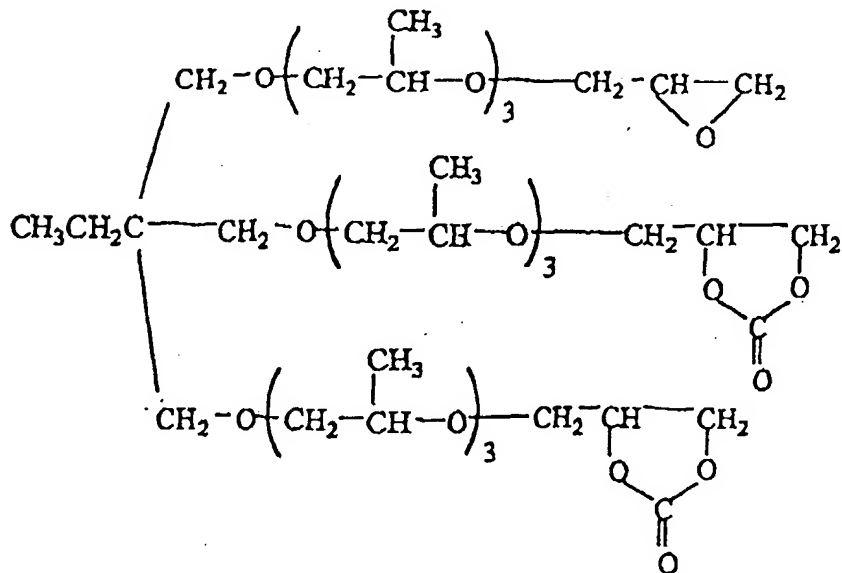
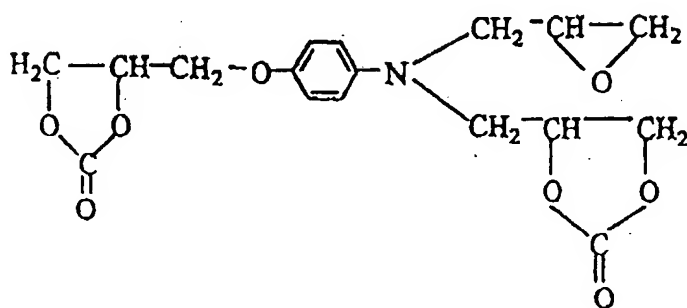
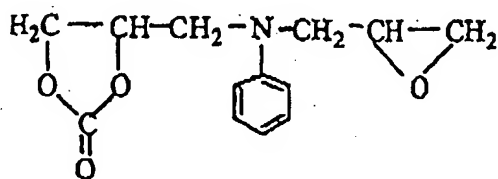
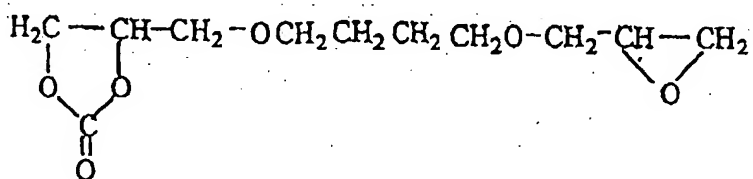
where: $R_{12}, R_{13} = \text{H, CH}_3$; $m + k = 0 - 6$, $n = 1$

19.

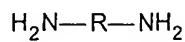
 $n = 1$  $n = 1$

5. The method according to p.2, includes preferably using oligomers, chosen from the following group:

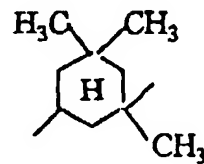
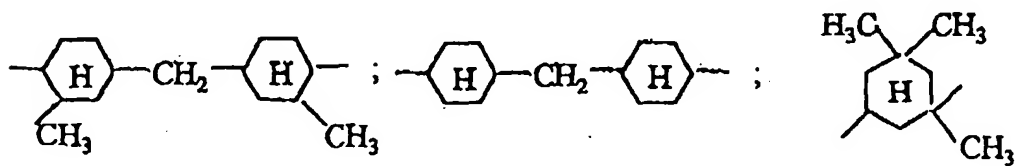
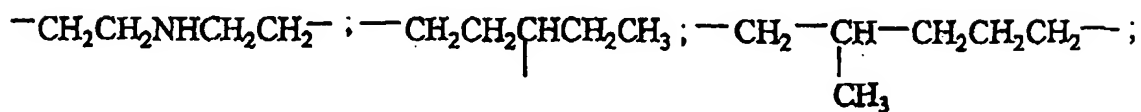
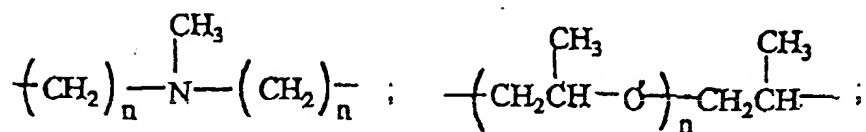
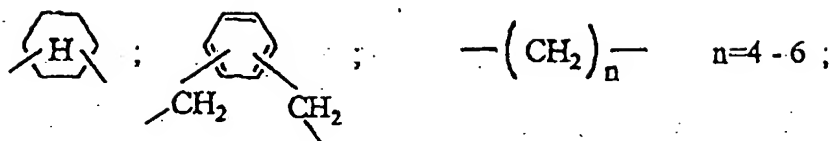




6. The method according to p.2, includes using aliphatic, cycloaliphatic diamines, chosen from the groups:



where R:





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 11 4308

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	DD 246 901 A (VEB) 24 June 1987 (1987-06-24) ---	1-6	C08G59/14 C08G59/18
A	DATABASE WPI Week 198251 Derwent Publications Ltd., London, GB; AN 1982-11341j XP002127912 & SU 908 769 A (FIGOVSKIT), 28 February 1982 (1982-02-28) * abstract * -----	1-6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08G
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 18 January 2000	Examiner Andriollo, G
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ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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18-01-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DD 246901 A		NONE	
SU 908769 A	28-02-1982	NONE	

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